OIPE JC177
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DECLARATION

I, Atsuko Ikeda, residing at 26-2-906, Ojima 3-chome, Koto-ku, Tokyo, Japan, do hereby certify that I am conversant with the English and Japanese languages and am a competent translator thereof. I further certify that to the best of my knowledge and belief the attached English translation is a true and correct translation made by me of U.S. Provisional Patent Application No. 60/216,519 filed on July 6, 2000.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 27th day of October, 2000

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[NAME OF DOCUMENT] Specification

[TITLE OF THE INVENTION]

Method and Apparatus for Measuring Halogen Concentration and Manufacturing Method for Halogen Compound

[SCOPE OF CLAIM FOR PATENT]

[Claim 1] A method for continuously measuring a halogen concentration, comprising continuously introducing a gas containing a halogen gas into a continuously flowing solution containing a metal iodide to produce iodine and measuring the intensity of a visible ray in a specific wavelength region transmitted through said solution, thereby continuously quantitating the iodine produced.

[Claim 2] The method for continuously measuring a halogen concentration as claimed in claim 1, wherein said solution containing a metal iodide contains starch.

[Claim 3] The method for continuously measuring a halogen concentration as claimed in claim 1, wherein said specific wavelength region is from 460 nm to 520 nm.

[Claim 4] The method for continuously measuring a halogen concentration as claimed in claim 2, wherein said specific wavelength region is from 580 nm to 780 nm.

[Claim 5] The method for continuously measuring a halogen concentration as claimed in claim 3 or 4, wherein

said visible ray is a laser ray.

[Claim 6] The method for continuously measuring a halogen concentration as claimed in any one of claims 1 to 5, wherein said halogen gas is chlorine gas or fluorine gas.

[Claim 7] An apparatus for continuously measuring a halogen concentration, which is used in the method for measuring a halogen concentration described in claim 1, said apparatus comprising a reaction part for producing iodine, a liquid feeding pump for continuously introducing a solution containing a metal iodide into said reaction part, an inlet pipe for sampling a part of the reaction gas containing a halogen gas from the production line of a halogen compound, a gas flow rate controller for continuously introducing a gas containing a halogen gas into said reaction part, which is connected to said inlet pipe, a gas-liquid separation part for separating an insoluble gas, a measuring part for measuring the iodine produced in said reaction part, which comprises a visible light source of emitting a visible ray and a detector for measuring the intensity of a visible ray transmitted, and a data processing part.

[Claim 8] An apparatus for continuously measuring a halogen concentration, which is used in the method for measuring a halogen concentration described in claim 2,

said apparatus comprising a reaction part for producing iodine, a liquid feeding pump for continuously introducing a solution containing a metal iodide and starch into said reaction part, an inlet pipe for sampling a part of the reaction gas containing a halogen gas from the production line of a halogen compound, a gas flow rate controller for continuously introducing a gas containing a halogen gas into said reaction part, which is connected to said inlet pipe, a gas-liquid separation part for separating an insoluble gas, a measuring part for measuring iodine produced in said reaction part, which comprises a visible light source of emitting a visible ray and a detector for measuring the intensity of a visible ray transmitted, and a data processing part.

[Claim 9] The apparatus for continuously measuring a halogen concentration as claimed in claim 7 or 8, wherein said visible light source is a laser.

[Claim 10] The apparatus for continuously measuring a halogen concentration as claimed in claim 9, wherein said laser is a semiconductor laser.

[Claim 11] A method for manufacturing a halogen compound, comprising reacting an organic compound with a halogen gas in the gaseous phase, wherein the halogen concentration is adjusted using the method for continuously

measuring a halogen concentration described in any one of claims 1 to 6.

[Claim 12] The method for manufacturing a halogen compound as claimed in claim 11, wherein said halogen gas is chlorine gas or fluorine gas.

[Claim 13] The method for manufacturing a halogen compound as claimed in claim 11 or 12, wherein said organic compound is at least one hydrofluorocarbon represented by formula (1):

$$C_aH_bF_c \qquad (1)$$

(wherein a, b and c each represents an integer satisfying the conditions of $1 \leqq a \leqq 3$, $1 \leqq b \leqq 4$, $1 \leqq c \leqq 7$, b+c=4 when a is 1, b+c=6 when a is 2, and b+c=8 when a is 3) and/or at least one fluorinated olefin represented by formula (2):

$$C_dH_eF_f \qquad (2)$$

(wherein d, e and f each represents an integer satisfying the conditions of $2 \leqq d \leqq 3$, $0 \leqq e \leqq 5$, $1 \leqq f \leqq 6$, e+f=4 when d is 2, and e+f=6 when d is 3), and said halogen gas is fluorine gas.

[Claim 14] The method for manufacturing a halogen compound as claimed in claim 13, wherein said hydrofluorocarbon is at least one selected from the group consisting of trifluoromethane, 1,1,1,2-tetrafluoroethane, pentafluoroethane, hexafluoropropane and heptafluoropropane.

[Claim 15] The method for manufacturing a halogen compound as claimed in claim 13, wherein said fluorinated olefin is at least one selected from the group consisting of tetrafluoroethylene, trifluoroethylene and hexafluoropropene.

[Claim 16] The method for manufacturing a halogen compound as claimed in any one of claims 11 to 15, wherein the concentration of said fluorine gas is controlled to be lower than the explosion range.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a method and an apparatus for continuously measuring a halogen gas concentration, and a method for producing a halogen compound using the measuring method.

[0002]

[Background Art]

With respect to the method for measuring a halogen gas concentration, iodometry is conventionally known. In the iodometry, iodide ion as a weak reducing agent is oxidized by a halogen as a strong oxidizing agent and thereby converted into iodine and the iodine is titrated to indirectly quantitate the halogen. This is one of the most

widely used titration methods and by this, a halogen such as chlorine and fluorine, an oxygen acid salt thereof and the like can be quantitated.

[0003]

With respect to the measuring apparatus to which this iodometry is applied, JP-A-63-247655 (the term "JP-A" as used herein means an "unexamined published Japanese patent application") describes a fluorine measuring apparatus wherein fluorine is converted into iodine gas and the fluorine is determined using the properties of the iodine gas such that the light absorption coefficient is larger than that of fluorine gas and the maximum absorption coefficient of iodine gas is present in the visible ray. And this is a fluorine detecting apparatus comprising a converting unit for converting fluorine into iodine gas and a measuring part for determining the fluorine by optically measuring the iodine gas generated in the converting unit. To speak more specifically about the method of converting fluorine into iodine gas, the fluorine is converted into iodine gas in the converting unit which is constructed by a first reaction column filled with, for example, potassium chloride particles and a second reaction column filled with potassium iodide particles, where the fluorine gas is converted into chlorine in the first reaction column filled

with potassium chloride and the chlorine is flown into the second reaction column and reacted with potassium iodide to produce iodine (I_2).

[0004]

Also, a method of converting a halogen gas into a different gas and measuring the concentration of the gas to indirectly determine the halogen concentration is known. For example, JP-A-63-27736 describes an apparatus for measuring a gas concentration, which is constructed by a filler for converting fluorine gas into another gas capable of absorbing infrared ray, a gas cell having provided on both sides thereof an optical window for transmitting an infrared ray, a light source for emitting an infrared ray to enter through the optical window, a detector for receiving the light transmitted from the gas cell, and a densitometer for computing the concentration of the gas converted from the fluorine gas based on the output of the detector. For the filler, for example, sulfur obtained by pulverizing crystalline sulfur is used and this converts the fluorine gas into sulfur hexafluoride gas capable of absorbing an infrared ray.

[0005]

JP-B-4-6896 (the term "JP-B" as used herein means an "examined Japanese patent publication") describes a method

and an apparatus for measuring the concentration of an oxidative gas such as fluorine and nitrogen trifluoride. According to this method, the concentration of an oxidative gas in an excimer laser gas comprising a mixed gas of an inert gas and an oxidative gas is determined by contacting a reducing gas such as hydrogen, methane or silicon hydride gas with the excimer laser gas and measuring the intensity of emitted light (chemiluminescence) generated upon the chemical reaction with the oxidative gas. The apparatus for measuring the concentration of an oxidative gas comprises an inlet pipe for sampling a part of the excimer laser gas by providing a branch pipe on the excimer laser gas circulating line, a reaction vessel having sealed therein a reducing gas selected from hydrogen gas, methane gas, silicon hydride gas and a mixed gas thereof, of which one end is connected to the inlet pipe, a feeding pipe for feeding the reducing gas into the reaction vessel, a detecting unit for detecting the chemiluminescence generated upon reaction of the oxidative gas with the reducing gas and converting it into electric signals, which is disposed at the other end of the reaction vessel opposing the laser gas inlet side, an amplifier for amplifying the electric signals, and a recording unit for recording and storing the amplified signals.

[0006]

In all of these methods, the halogen gas is once converted into a different compound and the halogen concentration is indirectly determined by measuring the concentration of the compound converted from the halogen gas. The measuring apparatus employs a system of introducing a gas to be measured and a reaction gas from one side, for example, of a reaction chamber and at the same time, sucking and exhausting the reacted gas from another side, but this has a problem in that unless a delicate valve operation well-balanced between introduction and exhaust is performed for maintaining the gas introduced to a constant amount, the measurement cannot be attained with good accuracy. In addition, at the time when the analysis results are obtained, the halogen gas is actually further fluctuated, therefore, it is difficult to maintain the halogen gas concentration to the set value.

[0007]

During the production of a halogen compound, the reaction is preferably performed in many cases using a halogen gas in excess as compared with the substrate under the conditions such that the halogen gas always remains in the reaction gas. However, if the amount of halogen gas is too large, equipment is necessary for recovering the gas

and this is not profitable. A preferred amount of halogen gas is selected according to the substrate with which the halogen gas is reacted, the reaction temperature or the presence or absence of a catalyst, but the matter of importance in the continuous production process is to maintain the concentration within an appropriate range. With respect to the method for continuously measuring the concentration, for example, for continuously analyzing a fluorine gas concentration at the field in the plant, the following methods are known:

(1) a fluorine detector using an electrochemical cell, and

(2) a method of automatically performing a series of operations of blowing an objective gas into an aqueous potassium iodide solution and titrating iodine generated upon reaction with fluorine gas by using sodium thiosulfate.

[0008]

The method of (1) is effective for temporarily measuring a fluorine-containing gas in a low concentration but when a fluorine-containing gas is continuously analyzed, the cell deteriorates within a short time, therefore, this method is not effective in attaining the object of the present invention. The method of (2) in which an ordinary method for analyzing fluorine contained in a gas is

automated, is disadvantageous in that it takes a time to obtain the results, the response rate is low, the maintenance is cumbersome and a fairly large space is necessary for installing the equipment.

[0009]

JP-A-2000-22255 describes a method for continuously analyzing a fluorine gas concentration. According to this method, the fluorine gas concentration is stably controlled at real time by directly measuring the concentration of fluorine gas in a mixed gas. This is used for measuring the concentration of a mixed gas containing fluorine gas, for example, a gas used in an excimer laser apparatus and detects the fluorine gas concentration from the change in the ultraviolet absorption of the fluorine gas in the mixed gas. The mixed gas used contains, in addition to the fluorine gas, for example, Kr gas or Ne gas and has a fluorine gas concentration of 1.0% or 9.0%.

[0010]

However, when this method is used for measuring a fluorine gas concentration during the production of a fluorine compound, there arises a problem. In the step of fluorinating hydrocarbon or hydrofluorocarbon by fluorine gas to produce perfluorocarbon, a very large heat of reaction is generated. The heat of reaction is proportional

to the molar number of fluorine used and as the amount of fluorine is larger, the heat of reaction becomes larger. Due to this generation of heat, breakage of C-C bond or explosion readily takes place or the yield decreases, giving rise to problems in the industrial production or operation. Therefore, for preventing abrupt generation of reaction heat in the direct fluorination reaction using fluorine gas, the fluorine gas is diluted with another inert gas (e.g., nitrogen, helium). In addition, since the gas after the reaction contains perfluorocarbon, which is the reaction product, and hydrogen fluoride equimolar to hydrogen displaced, the fluorine concentration is considerably low. Although it may depend on the value of absorption maximum wavelength (λ_{max}/nm) and molar absorption coefficient of the component gases contained, the absorption strength of a mixed gas having a low fluorine concentration and greatly prone to the effect of other gases contained therein is difficult to continuously determine.

[0011]

[Problems to be Solved by the Invention]

The present invention has been made under these circumstances and the object of the present invention is to provide a method for rapidly and easily measuring a halogen

gas with good accuracy and thereby controlling the halogen concentration to a set range, which is necessary for controlling the halogen gas in the plant of producing a halogen compound, and also provide a measuring apparatus for use in the measuring method, which has a compact structure and ensures quick and easy exchange of parts, and a method for producing a halogen compound using the measuring method.

[0012]

[Means to Solve the Problems]

As a result of extensive investigations to solve the above-mentioned problems, the present inventors have found that when a visible ray is irradiated on a solution containing iodine continuously generated and the intensity of transmitted light is continuously measured, a halogen gas concentration can be continuously measured, and also found a measuring apparatus for use in the measuring method and a method for manufacturing a halogen compound. The present invention has been accomplished based on these findings. The present invention provides a method and an apparatus for continuously analyzing a halogen concentration and a method for manufacturing a halogen compound using the measuring method, described in (1) to (16) below.

[0013]

(1) A method for continuously measuring a halogen concentration, comprising continuously introducing a gas containing a halogen gas into a continuously flowing solution containing a metal iodide to produce iodine and measuring the intensity of a visible ray in a specific wavelength region transmitted through the solution, thereby continuously quantitating the iodine produced.

(2) The method for continuously measuring a halogen concentration as described in (1) above, wherein the solution containing a metal iodide contains starch.

(3) The method for continuously measuring a halogen concentration as described in (1) above, wherein the specific wavelength region is from 460 nm to 520 nm.

(4) The method for continuously measuring a halogen concentration as described in (2) above, wherein the specific wavelength region is from 580 nm to 780 nm.

(5) The method for continuously measuring a halogen concentration as described in (3) or (4) above, wherein the visible ray is a laser ray.

[0014]

(6) The method for continuously measuring a halogen concentration as described in any one of (1) to (5) above, wherein the halogen gas is chlorine gas or fluorine gas.

(7) An apparatus for continuously measuring a halogen concentration, which is used in the method for measuring a halogen concentration described in (1) above, the apparatus comprising a reaction part for producing iodine, a liquid feeding pump for continuously introducing a solution containing a metal iodide into the reaction part, an inlet pipe for sampling a part of the reaction gas containing a halogen gas from the production line of a halogen compound, a gas flow rate controller for continuously introducing a gas containing a halogen gas into the reaction part, which is connected to the inlet pipe, a gas-liquid separation part for separating an insoluble gas, a measuring part for measuring the iodine produced in the reaction part, which comprises a visible light source of emitting a visible ray and a detector for measuring the intensity of a visible ray transmitted, and a data processing part.

(8) An apparatus for continuously measuring a halogen concentration, which is used in the method for measuring a halogen concentration described in (2) above, the apparatus comprising a reaction part for producing iodine, a liquid feeding pump for continuously introducing a solution containing a metal iodide and starch into the reaction part, an inlet pipe for sampling a part of the reaction gas containing a halogen gas from the production line of a

halogen compound, a gas flow rate controller for continuously introducing a gas containing a halogen gas into the reaction part, which is connected to the inlet pipe, a gas-liquid separation part for separating an insoluble gas, a measuring part for measuring iodine produced in the reaction part, which comprises a visible light source of emitting a visible ray and a detector for measuring the intensity of a visible ray transmitted, and a data processing part.

(9) The apparatus for continuously measuring a halogen concentration as described in (7) or (8) above, wherein the visible light source is a laser.

(10) The apparatus for continuously measuring a halogen concentration as described in (9) above, wherein the laser is a semiconductor laser.

[0015]

(11) A method for manufacturing a halogen compound, comprising reacting an organic compound with a halogen gas in the gaseous phase, wherein the halogen concentration is adjusted using the method for continuously measuring a halogen concentration described in any one of (1) to (6) above.

(12) The method for manufacturing a halogen compound as described in (11) above, wherein the halogen gas is

chlorine gas or fluorine gas.

(13) The method for manufacturing a halogen compound as described in (11) or (12) above, wherein the organic compound is at least one hydrofluorocarbon represented by formula (1):

$$C_aH_bF_c \qquad (1)$$

(wherein a, b and c each represents an integer satisfying the conditions of $1 \leqq a \leqq 3$, $1 \leqq b \leqq 4$, $1 \leqq c \leqq 7$, b+c=4 when a is 1, b+c=6 when a is 2, and b+c=8 when a is 3) and/or at least one fluorinated olefin represented by formula (2):

$$C_dH_eF_f \qquad (2)$$

(wherein d, e and f each represents an integer satisfying the conditions of $2 \leqq d \leqq 3$, $0 \leqq e \leqq 5$, $1 \leqq f \leqq 6$, e+f=4 when d is 2, and e+f=6 when d is 3), and the halogen gas is fluorine gas.

(14) The method for manufacturing a halogen compound as described in (13) above, wherein the hydrofluorocarbon is at least one selected from the group consisting of trifluoromethane, 1,1,1,2-tetrafluoroethane, pentafluoroethane, hexafluoropropane and heptafluoropropane.

(15) The method for manufacturing a halogen compound as described in (13) above, wherein the fluorinated olefin is at least one selected from the group consisting of tetrafluoroethylene, trifluoroethylene and hexa-

fluoropropene.

(16) The method for manufacturing a halogen compound as described in any one of (11) to (15) above, wherein the concentration of the fluorine gas is controlled to lower than the explosion range.

[0016]

To be brief, the present invention provides "a method for continuously measuring a halogen concentration by irradiating a visible ray to a solution containing iodine continuously generated and measuring the intensity of a ray transmitted", "an apparatus for use in the measuring method, in which the amount of iodine continuously generated in the reaction part is quantitated by continuously measuring the intensity of a visible ray transmitted" and "a method for manufacturing a halogen compound, where the halogen concentration is controlled using the measuring method".

[0017]

[Mode for Carrying Out the Invention]

As described above, when a halogenation reaction is performed using a halogen gas, the matter of importance is to maintain the concentration of a halogen gas remaining in the reaction gas in a proper range. The present invention has the following capabilities (1) to (3):

(1) a halogen gas of several thousands of ppm or less

can be stably measured over a long period of time without requiring any maintenance,

(2) the space necessary for the installation is small, and

(3) the response rate is high and the results can be fed back to the control in the production process,

so that a halogen gas concentration can be continuously measured with good response in the plant of producing a halogen compound.

[0018]

The present invention is described in detail below.

The method for measuring a halogen concentration of the present invention employs a known reaction such that an oxidizing agent such as fluorine and chlorine is contacted with an aqueous solution containing a metal iodide, then the metal iodide reacts with the oxidizing agent to generate iodine, and the iodine produced is quantitated, thereby indirectly measuring the halogen concentration. The metal iodide is preferably potassium iodide. The aqueous solution in which iodine is generated has a yellow color when the . concentration is low and as the iodine concentration elevates, the aqueous solution turns reddish yellow. Furthermore, when starch is added to the aqueous metal iodide solution, the starch acts on the iodine

generated and the aqueous solution is colored blue. On this solution colored from yellow to blue, a visible ray in a specific wavelength region of blue to red is irradiated, the intensity of a visible ray transmitted according to the strength of the color formed is measured to quantitate the amount of iodine generated, and from the value obtained, the halogen concentration in the gas is determined.

[0019]

In the case of using an aqueous potassium iodide solution, color formation occurs in the region of yellow to reddish yellow due to iodine and by irradiating a ray in the region of blue to green selected from the wavelength range of 460 to 520 nm and measuring the intensity of a ray transmitted, the amount of iodine can be quantitated. When starch is added to the aqueous potassium iodide solution, the solution is colored blue, therefore, by irradiating a ray of red color selected from the wavelength range of 580 to 780 nm and measuring the intensity of a ray transmitted, the amount of iodine can be quantitated.

[0020]

Examples of the light source for emitting a visible ray which can be used include a tungsten lamp, a xenon lamp and a quartz iodine lamp. In addition, a light emitting diode or a laser diode now on use for various uses can be

used. Depending on the kind of the light source, the wavelenght is selected in combination with a spectroscope.

[0021]

The method for continuously analyzing a halogen concentration of the present invention is described below. A measuring method using a laser light source is described by taking the analysis of fluorine gas as an example.

The method for measuring a halogen concentration of the present invention comprises the following steps (1) to (5):

(1) an aqueous solution having added thereto potassium iodide or further added starch is flown at a constant flow rate into a reaction part and a process gas containing fluorine gas is blown thereinto to continuously generate iodine;

(2) the solution turns reddish yellow from yellow due to the iodine generated upon reaction between the fluorine gas and potassium iodide and when starch is added, the solution is colored blue;

(3) when a water-insoluble diluting gas such as nitrogen is contained in a large amount, the solution is subjected to gas-liquid separation and only the liquid layer is introduced into a density measuring part;

(4) in the density measuring part, a selected laser

ray is irradiated from the outside of a transparent pipe and by means of a laser ray-receiving part disposed in the opposite side, the intensity of a laser ray transmitted through the solution is measured; and

(5) from the correlation between the intensity of a laser ray transmitted and the amount of iodine generated, the fluorine concentration in the gas measured is calculated.

[0022]

In the present invention, the solution in which iodine is generated may be either an aqueous potassium iodide solution or the aqueous solution to which starch is added. Of these, an aqueous solution where potassium iodide and starch are added is preferred. In this case, the iodine solution is colored blue and a visible ray in the red region is irradiated. The visible ray is preferably a laser ray having good directivity and the light source is preferably a semiconductor laser. The wavelength can be selected from the wavelength region of 580 to 780 nm, preferably from the wavelength region of 600 to 700 nm.

[0023]

The concentration of iodine measured is preferably 3×10^{-3} mol/L or less. If the concentration is too high, stable measurement results cannot be obtained, accordingly,

the concentrations and amounts of potassium iodide and starch in the aqueous solution fed to the reaction part and the amount of gas fed to the reaction part are selected so as not to allow the iodine construction to exceed the above-mentioned range. The responsibility can be controlled by the amount of solution fed to the reaction part and the response time can be shortened by increasing the amount of solution fed.

[0024]

The apparatus for continuously measuring a halogen concentration of the present invention is described below.

Fig. 1 is a schematic view showing an analysis apparatus according to one practical embodiment of the present invention. In this embodiment, the metal iodide is potassium iodide, a halogen gas-containing gas is introduced into a solution where starch is added, and the visible light source is a semiconductor laser having a wavelength of 670 nm.

In Fig. 1, 4 is a reaction part where a mixture solution of potassium iodide and starch runs at a constant flow rate, 1 is a gas flow rate controller connected to an inlet pipe (not shown), for introducing a part of a process gas containing a halogen gas sampled using the inlet pipe from the production line of a halogen compound into the

reaction part 4 while controlling the flow rate, 5 is a gas-liquid separation part for separating a water-insoluble diluting gas such as nitrogen so as to prevent the measured values from fluctuating, and 7 is a halogen concentration-measuring part equipped with a laser emission controlling part 8, a laser emission part 9, an aqueous solution running part 10, a laser ray-receiving part 11, a transmitted laser ray intensity-measuring part 12 and a data processing part 13. The data processing part 13 may be connected to a display part for indicating a halogen concentration and to a printer for recording the concentration, whereby an alarm can be given when the halogen concentration exceeds the set range.

[0025]

The constructive materials of respective units are individually selected from appropriate corrosion resistant materials because corrosiveness greatly differs between the part where a gas flows and the part where a liquid runs. A metal material is used for the surface of inlet pipe, flow controlling part and reaction part, where a halogen gas-containing process gas flows, and the surface is preferably passivated using, for example, fluorine gas. For the part where a liquid runs, fluororesin is preferably used because the hydrogen halide solution is in a high concentration,

particularly in the case of fluorine, the hydrogen fluoride solution is corrosive. The measuring part where a visible ray transmits is required to have transparency, therefore, a copolymer of tetrafluoroethylene and perfluoroalkyl vinyl ether (PFA) is preferably used.

[0026]

The method of manufacturing a halogen compound while controlling the halogen concentration using the analysis method of the present invention is described below.

Fig. 2 is a schematic view showing the production flow of a fluorine compound according to one practical embodiment of the present invention. In this embodiment, the flow shows the production of one compound or two different compounds in the production plant having two reaction zones. In Fig. 2, 21 is a first reaction zone where fluorine gas fed from 24 and hydrofluorocarbon fed from 25 are reacted; 22 is a second reaction zone where fluorine gas fed from 28 and hydrofluorocarbon fed from 29 are reacted using the reaction gas produced in the first reaction zone as a diluting gas; 31 is an outlet gas of the second reaction zone and a part of the gas, 33, introduced into a distillation and purification step and the remaining 32 is circulated and reused as the diluting gas in the first reaction zone and/or the second reaction zone; and 34

is a measuring apparatus shown in Fig. 1, which can measure and control the fluorine concentration in the whole production plant. In the case of a two-stage reaction shown in Fig. 2, the fluorine concentration can be more exactly controlled by disposing a measuring apparatus in each step and measuring the fluorine concentration.

[0027]

The hydrofluorocarbon is at least one of the hydrofluorocarbons represented by formula (1):

$$C_aH_bF_c \qquad (1)$$

(wherein a, b and c each represents an integer satisfying the conditions of $1 \leqq a \leqq 3$, $1 \leqq b \leqq 4$, $1 \leqq c \leqq 7$, b+c=4 when a is 1, b+c=6 when a is 2, and b+c=8 when a is 3). Among these, preferred are trifluoromethane, 1,1,1,2-tetrafluoroethane, pentafluoroethane, hexafluoropropane and heptafluoropropane.

[0028]

Instead of the above-mentioned hydrofluorocarbon, at least one of the fluorinated olefins represented by formula (2) may be used:

$$C_dH_eF_f \qquad (2)$$

(wherein d, e and f each represents an integer satisfying the conditions of $2 \leqq d \leqq 3$, $0 \leqq e \leqq 5$, $1 \leqq f \leqq 6$, e+f=4 when d is 2, and e+f=6 when d is 3). Among these, preferred are tetrafluoroethylene, trifluoroethylene and hexafluoro-

propene.

[0029]

In reacting the hydrofluorocarbon or fluorinated olefin with fluorine gas, it is necessary that the mixed gas composition does not fall in the range of explosion. Although the value may vary depending on the kind of the compound, each value is set to the safe range below the lower limit of explosion range.

[0030]

[Examples]

The present invention is described in greater detail below by referring to the Examples, however, the present invention should not be construed as being limited to these Examples.

(Preparation of Potassium Iodide-Starch Solution)

(1) Potassium Iodide Solution:

In 1 L of pure water, 10 g of potassium iodide was dissolved.

(2) Starch Solution:

To 200 ml of pure water, 1 g of starch was added, and the mixture was heated at 50°C, stirred and then left standing for 30 minutes. From the resulting solution, 100 ml of the supernatant was sampled and used as the starch solution.

(3) Potassium Iodide-Starch Solution:

To 99 ml of the potassium iodide solution prepared above, 1 ml of the starch solution was added to prepare a potassium iodide-starch solution.

[0031]

(Measurement of Iodine Concentration)

Using the apparatus shown in Fig. 1, the correlation between iodine concentration and output value of a red laser ray sensor was obtained. The results are shown in Table 1. Also, simulating the conditions in actual measurement, the potassium iodide-starch solution and a process gas were flown into a reaction part at 2 ml/min and 20 ml/min, respectively, and reacted. In this case, the iodine concentrations of the following three kinds of solutions correspond to the specific fluorine concentrations and these fluorine concentration values are shown together in Table 1. These are shown as the standard values in Fig. 3.

(1) A fluorine-containing gas was blown into the potassium iodide-starch solution to prepare three kinds of solutions different in the color. These solutions were titrated by sodium thiosulfate to measure the iodine concentration.

(2) These three kinds of solutions each was placed in

the measuring part of Fig. 1, a red laser ray at a wavelength of 670 nm was irradiated thereon, and the output value of the light sensor was measured.

[0032]

[Table 1]

Iodine Concentration (mol/L)	Output Value of Light Sensor (V)	Corresponding Fluorine Concentration (ppm)
7.6×10^{-4}	-0.903	1700
4.6×10^{-4}	-0.760	1100
2.3×10^{-4}	-0.630	500

[0033]

(Example 1)

In the continuous process of manufacturing tetrafluoromethane (FC-14) by directly fluorinating trifluoromethane (HFC-23) in the presence of a diluting gas, the reaction was performed under four different conditions and the fluorine gas concentration in each process gas was measured using the apparatus shown in Fig. 1. Likewise the above-described conditions, the measurement was performed by flowing the potassium iodide-starch solution and the process gas into the reaction part at 2 ml/min and 20 ml/min, respectively. The analysis of fluorine gas concentration was obtained from the output value of the light sensor. At the same time, a titration analysis by

sodium thiosulfate was performed to confirm the fluorine concentration. The results of the titration analysis by sodium thiosulfate and the output values of the light sensor are shown in Table 2 and Fig. 3. The output values of the light sensor are present on the straight line of the standard values shown in Fig. 3 and this reveals that the measured results of residual fluorine gas concentration have high reliability.

[0034]

[Table 2]

Fluorine Concentration (ppm)	Output of Light Sensor (V)
800	-0.710
2100	-0.930
3500	-1.040
6400	-1.160

[0035]

(Example 2)

This example is described using Fig. 2 which shows the flow in the manufacturing method of perfluorocarbon. Trifluoromethane as hydrofluorocarbon (numeral 25 in the figure) and fluorine gas (numeral 24 in the figure) were mixed with a diluting gas (numeral 32 in the figure), and the resulting mixed gas (numeral 26 in the figure) was introduced into a first reaction zone (numeral 21 in the

figure). In the first reaction zone, the reaction was performed under such conditions that the reaction pressure was 1.5 MPa, the reaction temperature was 400°C, the molar ratio of F2/trifluoromethane was 1.51 and the inlet trifluoromethane concentration was 2.1 mol%, and thereby an outlet gas (numeral 27 in the figure) of the first reaction zone was obtained.

[0036]

With this outlet gas, 1,1,1,2-tetrafluoroethane as a new hydrofluorocarbon (numeral 29 in the figure) and fluorine gas (numeral 28 in the figure) were mixed, and the resulting mixed gas (numeral 30 in the figure) was introduced into the second reaction zone (numeral 22 in the figure). In the second reaction zone, the reaction was performed under such conditions that the reaction pressure was 1.5 MPa, the reaction temperature was 370°C, the molar ratio of F2/1,1,1,2-tetrafluoroethane was 2.06 and the inlet tetrafluoroethane concentration was 1.35 mol%, and thereby an outlet gas (numeral 31 in the figure) of the second reaction zone was obtained. This outlet gas was divided into a diluting gas (numeral 32 in the figure) and a gas introduced into the distillation and purification step (numeral 33 in the figure). The results are shown in Table 3. In the Table, "No." corresponds to the number in

Fig. 2. In Table 3, the fluorine gas concentration of the component 33 was a value measured using the apparatus of Fig. 1 and this value finely agreed with the result in the titration analysis by sodium thiosulfate, verifying that fluorine gas in a low concentration can be continuously measured.

[0037]

[Table 3]

Component	24	25	26	27	28	29	30	31	32	33
F2	1.003		1.012	0.367	0.585		0.952	0.010	0.009	0.001
HFC-134a			0.004			0.462	0.462	0.004	0.004	
HFC-23		0.665	0.668	0.047			0.047	0.003	0.003	
HF			17.288	17.933			17.933	18.873	17.288	1.585
HFC-125			0.030	0.015			0.015	0.033	0.030	0.003
FC-116			4.983	5.002			5.002	5.440	4.983	0.457
FC-14			7.295	7.916			7.916	7.964	7.295	0.669
Others	0.010	0.001	0.031	0.031	0.007		0.038	0.038	0.020	0.018
Total	1.013	0.666	31.489	31.489	0.592	0.462	32.365	32.365	29.632	2.733

In the Table, each component is in the unit of Kmol/hr. In addition, in the Table, HFC-134a is 1,1,1,2-tetrafluoroethane, HFC-23 is trifluoromethane and HFC-125 is pentafluoroethane.

[0038]

[Effects of the Invention]

As described in the foregoing pages, according to the present invention, the amount of iodine generated upon reaction of a halogen with a metal iodide solution is determined by measuring the intensity of a visible ray transmitted and thereby the halogen concentration is indirectly determined, where the concentration of a halogen gas contained in a reaction gas can be continuously measured, though this is conventionally difficult to attain. Furthermore, when the measuring method of the present invention is used in the production plant of a halogen compound, the halogen concentration can be easily controlled to the amount necessary for the reaction and this is profitable. The method of the present invention can be adapted to the continuous measurement of the concentration not only of the halogen-containing gas but also of an aqueous solution of oxygen acid salt thereof or the like.

[BRIEF DESCRIPTION OF DRAWINGS]

[Fig. 1]

Fig. 1 is a schematic view showing an apparatus for analyzing a halogen concentration according to one embodiment of the present invention.

[Fig. 2]

Fig. 2 is a schematic view showing a production flow of perfluorocarbon according to one embodiment of the present invention.

[Fig. 3]

Fig. 3 is a view showing the correlation between fluorine concentration and output value of the light sensor according to one embodiment of the present invention.

[Description of Reference Numerals]

1 gas flow rate controller

3 liquid feeding pump

4 reaction part

5 gas-liquid separation part

7 halogen concentration measuring part

8 laser emission controlling part

9 laser emission part

10 aqueous solution running part

11 laser ray-receiving part

12 transmitted laser ray intensity-measuring part

13 data processing part

21 first reaction zone

22 second reaction zone

23 distillation and purification step

24 fluorine gas fed to first reaction zone

25 hydrofluorocarbon fed to first reaction zone

26 gas components fed to first reaction zone

27 outlet gas components of first reaction zone

28 fluorine gas fed to second reaction zone

29 hydrofluorocarbon fed to second reaction zone

30 gas components fed to second reaction zone

31 outlet gas components of second reaction zone

32 diluting gas

33 gas introduced to distillation and purification step

34 fluorine gas concentration measuring apparatus

[NAME OF THE DOCUMENT] Abstract

[SUMMARY]

[PROBLEM TO BE SOLVED]

To provide a method for continuously measuring a halogen gas in the rapid and easy manner with good accuracy and thereby controlling the halogen concentration to a set range, which is necessary for controlling the halogen gas in the plant of producing a halogen compound, and also to provide an apparatus for continuously measuring a halogen gas, having a compact structure and ensuring quick and easy exchange of parts.

[MEANS TO SOLVE THE PROBLEM]

A halogen-containing gas is continuously introduced into a continuously flowing metal iodide-containing solution to produce iodine and the intensity of a visible ray in a specific wavelength region transmitted through the solution is measured, thereby continuously determining the halogen concentration.

[SELECTED DRAWING] None.

[NAME OF DOCUMENT] Drawings

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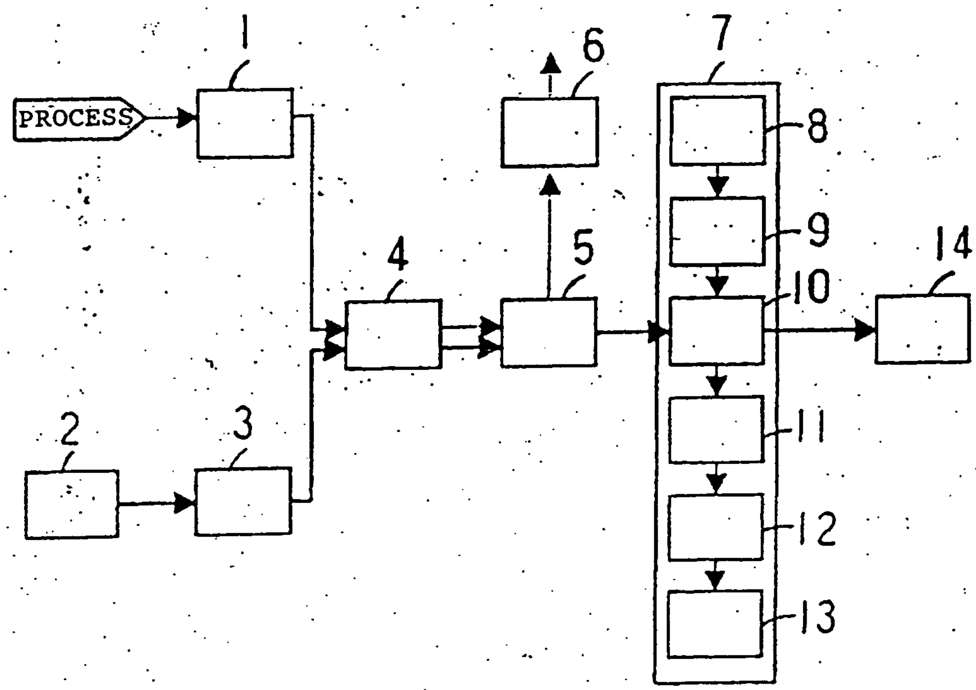
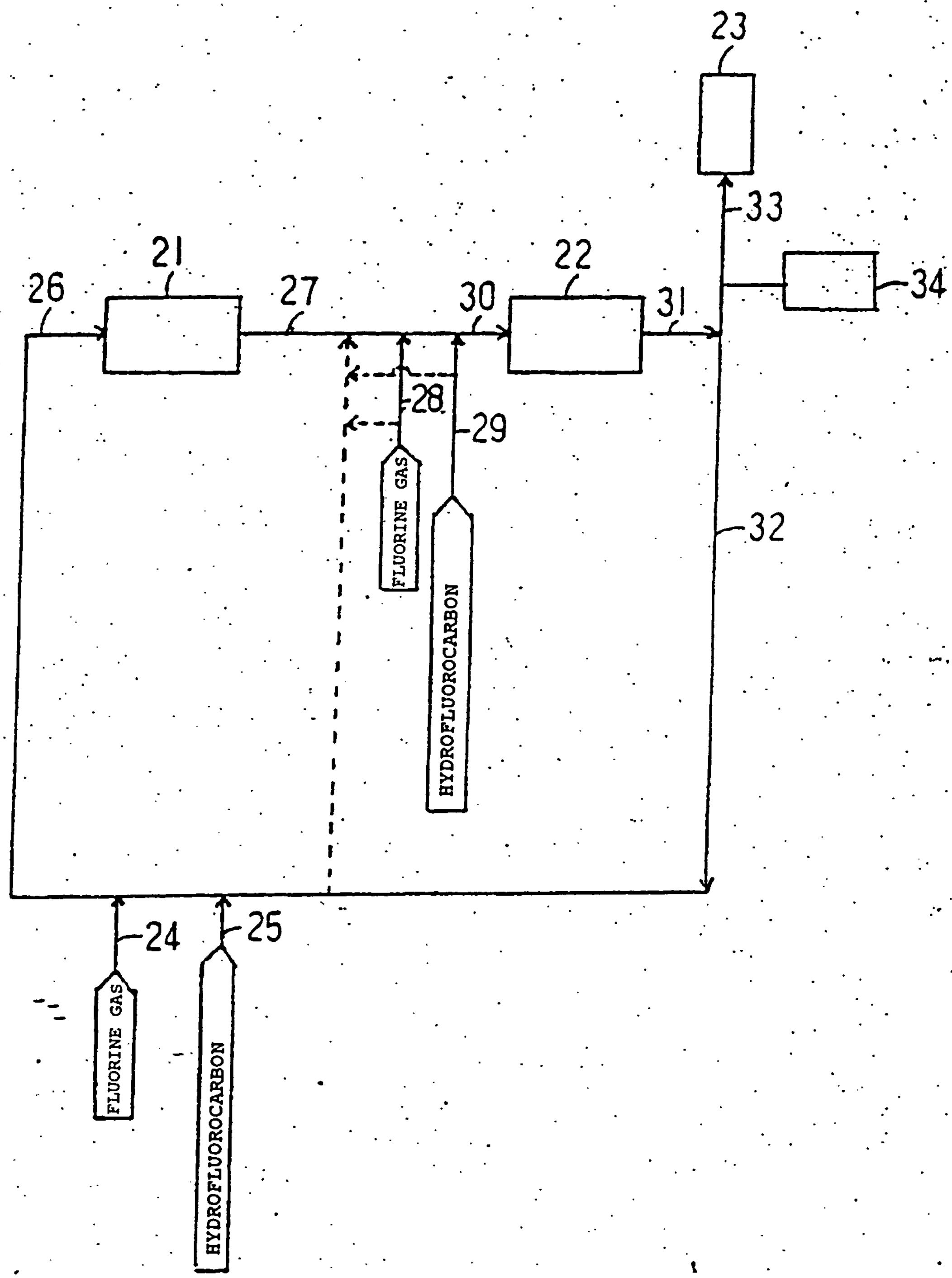
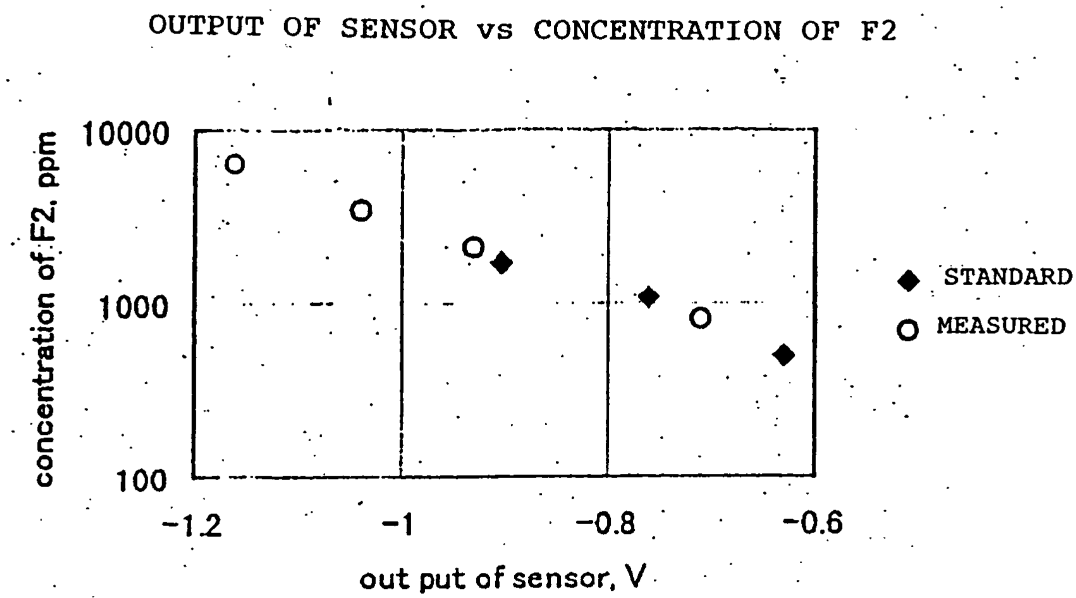
[Fig. 1]



[Fig. 2]


23
33
34
21
22
26
27
30
31
28
29
32
FLUORINE GAS
HYDROFLUOROCARBON
24
25
FLUORINE GAS
HYDROFLUOROCARBON

[Fig. 3]


OUTPUT OF SENSOR vs CONCENTRATION OF F2
10000
1000
100
concentration of F2, ppm
-1.2
-1
-0.8
-0.6
out put of sensor, V
STANDARD
MEASURED